

Toward N-heterocyclic carbene stabilized zinc sulfides

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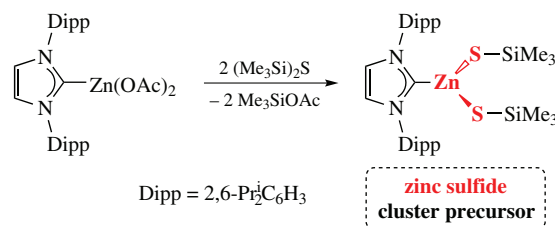
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A series of N-heterocyclic carbene (NHC) supported group 12 acetate complexes were prepared and their use as building blocks toward soluble group 12 sulfide precursors was explored. The highly moisture-sensitive NHC-ligated zinc dithiolato complex [(IPr)Zn(SSiMe₃)₂] was also synthesized [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], and its partial hydrolysis gave the dianionic zinc sulfide cluster [Zn₃(μ₃-S)(μ₂-SSiMe₃)₃(SSiMe₃)₃]²⁻, which contained a rare example of a Zn₃S structural motif. This preliminary observation indicates that the future growth of related metallosulfide clusters from [(IPr)Zn(SSiMe₃)₂] should be possible.



Keywords: silyl sulfides, zinc complexes, N-heterocyclic carbenes, group 12 elements, clusters, molecular precursors.

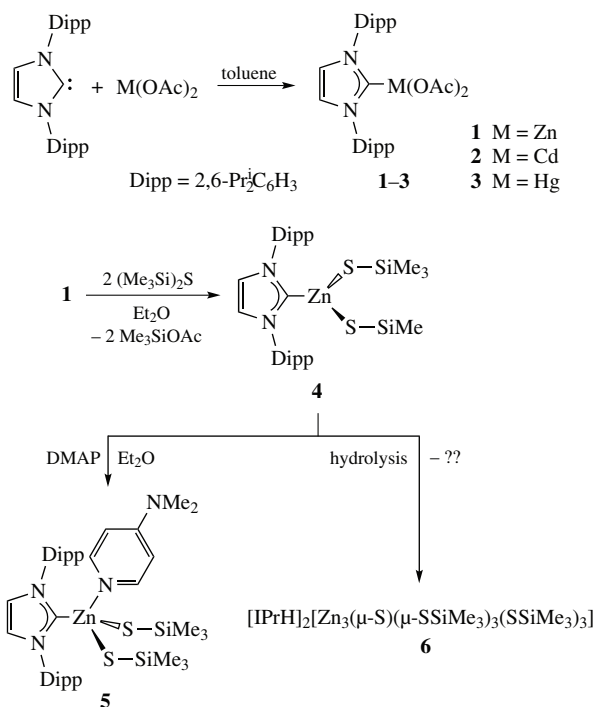
The group 12 elements zinc, cadmium and mercury are generally sourced from their metal sulfide ores: ZnS (sphalerite), CdS (greenockite) and HgS (cinnabar).¹ Notably, these metal sulfides are direct band gap semiconductors and as such have garnered significant interest in the realm of materials science,² and in the case of Cu-doped ZnS, long-lived phosphorescence is possible.³ Despite the widespread exploration of group 12 sulfide nanoparticles, their syntheses typically rely on high temperature ‘hot-injection’ protocols and the use of toxic/reactive precursors such as CdMe₂.^{2(a)} Thus, it would be of value to devise new single-source (molecular) precursors to group 12 chalcogenides that are easier to handle. Given our group’s previous use of ligand-stabilized GeH₂ complexes for the controlled formation of Ge nanoparticles and films under mild conditions from solution (typically at 100–150 °C),⁴ we looked to utilize a similar approach to yield soluble molecular group 12 metal sulfide precursors. Of particular relevance to this study, several group 12 complexes containing metal-sulfide bonds [M(SR)₂]_x (M = Zn, Cd, Hg; R = alkyl or aryl groups) involving bulky thiolato ligands have been prepared,⁵ while neutral donor-stabilized binary metal sulfides have yet to be isolated. We were also encouraged by a report from the Corrigan group, wherein the N-heterocyclic carbene ligand, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), was used to prepare a series of novel luminescent clusters of the general formula [(IPr)₄Au₄E₄Ch₄] (E = Ag or Au; Ch = S, Se, Te).⁶ Given the aforementioned use of the IPr ligand to prepare metallochalcogen clusters,⁶ we decided to make group 12 metal sulfides [(IPr)M(S)]_x (M = Zn, Cd, Hg) a synthetic target. This communication documents our initial efforts in this regard.

It was reasoned that the desired group 12 sulfide complexes [(IPr)M(S)]_x (M = Zn, Cd, Hg) could be synthesized by first preparing [(IPr)M(SSiMe₃)₂], followed by the addition of [(IPr)MX₂] (with concomitant Me₃SiX elimination; X = halide). A related 2014 study by Maron, Okuda and coworkers communicated

the preparation of the NHC-stabilized thiolate-bridged cationic cluster [(IMes)₂Zn₂(μ-SPh)₃]⁺ by addition of PhSSPh to the dicationic cluster [(IMes)₃Zn₃H₄(THF)]²⁺.⁷ We began our own investigations by first surveying the reaction of known IPr-supported zinc dihalide compounds [(IPr)ZnX₂] (X = Cl, I)⁸ with the sulfur atom sources (Me₃Si)₂S and Li[SSiMe₃].⁹ Unfortunately, product mixtures were obtained in all cases, with no evidence for the formation of the desired zinc(II) thiolato complex [(IPr)Zn(SSiMe₃)₂] by ¹H NMR spectroscopy. We then turned to the previously reported¹⁰ IPr-ligated zinc dihydride dimer [(IPr)ZnH(μ-H)]₂ and explored its reactivity with (Me₃Si)₂S. Analysis of the ¹H NMR spectrum revealed the sluggish formation of a new product, exhibiting resonances that corresponded to a new IPr species with two NMR equivalent -SiMe₃ groups (δ = 0.33 ppm), consistent with the formation of the target complex [(IPr)Zn(SSiMe₃)₂]. Unfortunately, this reaction was prohibitively slow, even with a tenfold excess of (Me₃Si)₂S, providing a very low conversion to the desired product (<10% by ¹H NMR spectroscopy) after stirring for 16 h. The formation of [(IPr)Zn(SSiMe₃)₂] was never able to reach completion as competing decomposition of the zinc dihydride precursor occurs at room temperature in solution, leading to the dihydroaminal IPrH₂ (ref. 11) and metallic zinc.^{10(b)}

Taking inspiration from the previously reported syntheses of [L–Zn(SSiMe₃)₂] systems (L = tetramethylethylenediamine or 3,5-lutidine) via zinc acetate precursors,¹² we looked to use the carbene-substituted adducts [(IPr)M(OAc)₂] (M = Zn, Cd, or Hg) to advance our chemistry, however these acetate complexes had yet to be reported in the literature.[†] Fortunately, we found that addition of IPr to the metal acetates M(OAc)₂ (M = Zn, Cd, Hg) in toluene afforded complexes [(IPr)Zn(OAc)₂] **1**, [(IPr)Cd(OAc)₂] **2** and [(IPr)Hg(OAc)₂] **3** in high yields

[†] A structurally related carbene-zinc carboxylate [(IMes)Zn(O₂CBu^t)₂] [IMes = (HCNMe)₂C; Mes = 2,4,6-Me₃C₆H₂] was reported recently.¹³



Scheme 1

(Scheme 1, top) as sparingly soluble white solids. Despite repeated attempts to crystallize **1–3**, we could not obtain crystals of sufficient quality for X-ray crystallography, however each species gave NMR spectra consistent with the assigned chemical formula, while compounds **1** and **3** also gave satisfactory elemental analyses. Interestingly, $^4J_{\text{H-Hg}}$ coupling (32.2 Hz in CDCl_3) could be discerned in the ^1H NMR spectrum of complex **3**, corresponding to coupling between an olefinic C–H proton in the carbene ligand backbone and the Hg center; similar $^4J_{\text{H-Hg}}$ coupling was found in $[(\text{IPr})\text{HgCl}_2(\text{HgCl}_2)_2]$.¹⁴ Of added note, compounds **1–3** are highly thermally stable ($>250\text{ }^\circ\text{C}$) and should serve as excellent building blocks to group 12 clusters in the future.¹⁵

Gratifyingly, we found that the combination of the zinc acetate complex $[(\text{IPr})\text{Zn}(\text{OAc})_2]$ **1** with two equivalents of $(\text{Me}_3\text{Si})_2\text{S}$ resulted in the quantitative formation of the highly moisture-sensitive compound $[(\text{IPr})\text{Zn}(\text{SSiMe}_3)_2]$ **4** (see Scheme 1, middle). X-ray crystallography confirmed the expected atomic connectivity and monomeric nature of **4**, however we were unable to grow crystals of suitable quality for a more complete analysis of the bonding situation in this thermally stable solid (mp $138\text{--}142\text{ }^\circ\text{C}$). Colorless X-ray quality crystals of compound $[(\text{IPr})\text{Zn}(\text{SSiMe}_3)_2(\text{DMAP})]$ **5** (Figure 1)[‡] were obtained by layering a solution of **4** in fluorobenzene with

[‡] Crystals of compound **5** were grown by storing a fluorobenzene solution at $-30\text{ }^\circ\text{C}$ for three weeks. Crystals of compound **6** were grown by storing a toluene solution of **4** layered with hexanes at $-30\text{ }^\circ\text{C}$ overnight.

Crystal data for 5. $\text{C}_{46}\text{H}_{69}\text{FN}_4\text{S}_2\text{Si}_2\text{Zn}$, $M = 882.72$, triclinic, space group $P\bar{1}$, 173.15 K , $a = 10.100(3)$, $b = 12.363(4)$ and $c = 21.191(7)\text{ \AA}$, $\alpha = 89.824(5)^\circ$, $\beta = 85.218(5)^\circ$, $\gamma = 69.150(5)^\circ$, $Z = 2$, $V = 2463.2(14)\text{ \AA}^3$, $d_{\text{calc}} = 1.190\text{ g cm}^{-3}$, $F(000) = 944$. Colorless block-shaped crystal with dimensions $0.29 \times 0.14 \times 0.12\text{ mm}$ was selected and intensities of 18595 reflections were measured using a Bruker D8/APEX II CCD diffractometer (ω scans, $\lambda[\text{MoK}\alpha] = 0.71073\text{ \AA}$, $\mu = 0.670\text{ mm}^{-1}$, $2\theta_{\text{max}} = 51.65^\circ$). After merging of equivalents and absorption correction, 9384 independent reflections ($R_{\text{int}} = 0.0637$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0687$ [6330 reflections with $I > 2\sigma(I)$], $wR_2 = 0.2017$ (all reflections), $\text{GOF} = 0.993$.

Crystal data for 6. $\text{C}_{79}\text{H}_{136}\text{N}_4\text{S}_7\text{Si}_6\text{Zn}_3$, $M = 1730.98$, monoclinic, space group $P2_1/c$, 173.15 K , $a = 15.6474(3)$, $b = 20.7512(3)$ and $c = 30.1314(5)\text{ \AA}$, $\beta = 92.7671(9)^\circ$, $Z = 4$, $V = 9772.3(3)\text{ \AA}^3$,

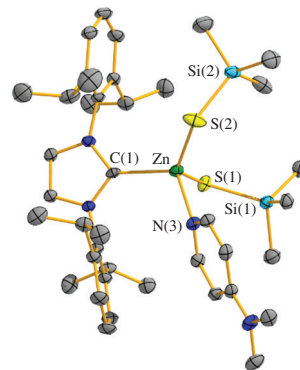


Figure 1 Molecular structure of $[(\text{IPr})\text{Zn}(\text{SSiMe}_3)_2(\text{DMAP})]$ **5** with thermal ellipsoids plotted at the 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): $\text{C}(1)\text{--Zn}$ 2.094(4), $\text{Zn--S}(1)$ 2.317(1), $\text{Zn--S}(2)$ 2.296(1), $\text{Zn--N}(3)$ 2.126(3); $\text{S}(1)\text{--Zn--S}(2)$ 128.07(5), $\text{S}(1)\text{--Zn--N}(3)$ 103.62(9), $\text{S}(1)\text{--Zn--C}(1)$ 100.45(10).

a fluorobenzene solution of 4-dimethylaminopyridine (DMAP), followed by cooling to $-30\text{ }^\circ\text{C}$. Despite growing X-ray quality crystals, contamination of the bulk product with free IPr was consistently found. The zinc center in **5** adopts an expected distorted tetrahedral coordination geometry with a $\text{C}_{\text{IPr}}\text{--Zn}$ bond length [$2.094(4)\text{ \AA}$] in the range of typical four-coordinate IPr-bound zinc species (*cf.* $2.042(2)\text{ \AA}$ in $[(\text{IPr})\text{ZnI}_2(\text{THF})]$)^{8(b)} as well as a $\text{N}_{\text{DMAP}}\text{--Zn}$ distance of $2.126(3)\text{ \AA}$. The Zn--S lengths in **5** average to $2.306(1)\text{ \AA}$ and lie in the range of Zn--S single bonds [$2.184(5)\text{--}2.371(5)\text{ \AA}$] found in Bochmann's zinc(II) thiolate dimer $[\text{Zn}(\text{SMes}^*)(\mu\text{-SMes}^*)_2]$ ($\text{Mes}^* = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$).^{5(a)} While compound **4** is stable for several days in solution, we found that **5** would decompose in C_6D_6 at room temperature to give free IPr and unidentified insoluble precipitate(s) (*ca.* 30% decomposition after 1 h).

In an attempt to crystallize complex **4**, a saturated toluene solution of this species was layered with hexanes and stored at $-30\text{ }^\circ\text{C}$ overnight, yielding a few small colorless crystals. X-ray crystallographic analysis revealed the crystals to be the dianionic zinc sulfide cluster salt $[\text{IPrH}_2][\text{Zn}_3(\mu_3\text{-S})(\mu_2\text{-SSiMe}_3)_3(\text{SSiMe}_3)_3]$ **6** (Figure 2).[‡] This species was likely formed by the partial hydrolysis of **4** with adventitious water and was obtained in subsequent attempts to crystallize **4** (albeit inconsistently and in very small yield). This cluster features an unusual Zn_3S capping motif with $\mu_3\text{-S}$ bonding [atom S(7) in Figure 2] and suggests that **4** may indeed act as a molecular precursor to other molecular zinc sulfide clusters under the appropriate reaction conditions; a search of the Cambridge Structural Database (CSD) revealed that the dianion in **6** is the first tri-zinc cluster with a capping $\mu_3\text{-sulfide}$. Related salts containing the homoleptic zincate $[\text{Zn}(\text{SSiMe}_3)_3]^-$ anion

$d_{\text{calc}} = 1.177\text{ g cm}^{-3}$, $F(000) = 3696$. Colorless crystal fragment with dimensions $0.42 \times 0.09 \times 0.07\text{ mm}$ was selected and intensities of 69438 reflections were measured using a Bruker D8/APEX II CCD diffractometer (ω and ϕ scans, $\lambda[\text{CuK}\alpha] = 1.54178\text{ \AA}$, $\mu = 3.248\text{ mm}^{-1}$, $2\theta_{\text{max}} = 150.07^\circ$). After merging of equivalents and absorption correction, 19762 independent reflections ($R_{\text{int}} = 0.0392$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0363$ [16044 reflections with $I > 2\sigma(I)$], $wR_2 = 0.0956$ (all reflections), $\text{GOF} = 1.040$.

The structures were solved by intrinsic phasing and refined by full-matrix least-squares on F^2 in anisotropic approximation. All calculations were carried out with SHELXT¹⁷ (structure solution) and SHELXL¹⁸ (structure refinement) programs. Molecular graphics were drawn using Diamond.¹⁹

CCDC 2047363 and 2047364 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* <http://www.ccdc.cam.ac.uk>.

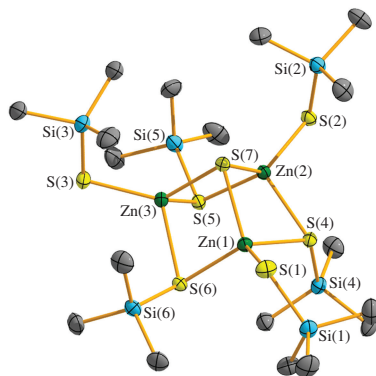


Figure 2 Molecular structure of the dianionic cluster $[\text{Zn}_3(\mu_3\text{-S})(\mu_2\text{-SSiMe}_3)_3(\text{SSiMe}_3)_3]^{2-}$ in **6** with thermal ellipsoids plotted at the 30% probability level. All H atoms and the two $[\text{IPrH}]^+$ counterions have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Zn(1)–S(4) 2.4289(6), Zn(1)–S(6) 2.4025(6), Zn(3)–S(5) 2.4655(6), Zn(3)–S(6) 2.4710(6), Zn(2)–S(4) 2.4221(6), Zn(2)–S(5) 2.4371(6), Zn(2)–S(7) 2.3572(6); S(1)–Zn(1)–S(4) 114.70(3), S(4)–Zn(1)–S(6) 108.22(2), S(4)–Zn(1)–S(7) 93.63(2).

were recently reported by Sundermeyer and coworkers.¹⁶ Our attempts to prepare a carbene-supported binary zinc sulfide $[(\text{IPr})\text{Zn}(\mu\text{-S})]_x$ by combining $[(\text{IPr})\text{Zn}(\text{SSiMe}_3)_2]$ **4** with an equimolar amount of $[(\text{IPr})\text{Zn}(\text{OAc})_2]$ **1** failed, instead affording free IPr in solution and an insoluble white precipitate (presumably zinc sulfide).

We then attempted to form the heavy element analogues of **4**, $[(\text{IPr})\text{Cd}(\text{SSiMe}_3)_2]$ and $[(\text{IPr})\text{Hg}(\text{SSiMe}_3)_2]$ starting from the precursors **2** and **3** (see Scheme 1), respectively. Upon addition of $(\text{Me}_3\text{Si})_2\text{S}$ to a slurry of **2** in toluene, the reaction mixture became mostly clear with the deposition of a fine white precipitate; ^1H NMR analysis of the recovered soluble fraction revealed the exclusive presence of the free carbene IPr. When $(\text{Me}_3\text{Si})_2\text{S}$ was added to a slurry of the Hg complex **3**, a dense orange solid formed, which became black after a few minutes of stirring; again, the only soluble species present according to ^1H NMR analysis was free IPr. This observation may be ascribed to the weaker nature of coordinative/dative $\text{NHC} \rightarrow \text{Cd}/\text{Hg}$ interactions in comparison to zinc,²⁰ whereby NHC dissociation in the heavier element systems leads to irreversible $[\text{M}(\text{SSiMe}_3)_2]_x$ aggregate formation (and/or decomposition). While late-transition metal NHC complexes are amenable to $\text{C}_{\text{NHC}}\text{-M}$ bond cleavage in the presence of sulfur-containing reagents,²¹ we did not observe the formation of any NHC-S coupling products (e.g. NHC=S) by ^1H NMR spectroscopy.

In conclusion, we have reported a series of N-heterocyclic carbene-supported group 12 acetates. The zinc(II) acetate adduct $[(\text{IPr})\text{Zn}(\text{OAc})_2]$ was found to be an effective building block¹³ for the formation of carbene-bound zinc dithiolato complexes. While only on a small scale, the formation of the trimetallic zinc-sulfur cluster $[\text{Zn}_3(\mu_3\text{-S})(\mu_2\text{-SSiMe}_3)_3(\text{SSiMe}_3)_3]^{2-}$ was obtained via the hydrolysis of **4**, showing promise that related clusters might be accessed in the future from the reported zinc dithiolato complexes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.009.

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